

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Structure and Intrinsic Stress of Platinum Films

R. E. ROTTMAYER and R. W. HOFFMAN, *J. Vacuum Sci. Technol.*, 1971, 8, (1), 151-155

Measurement of stress as a function of thickness in Pt thin films was made at 100-600°C. At 100°C the tensile value of the stress $\approx 10^{10}$ dyne/cm², but decreased sharply at 300°C to a very small value at 500°C and 600°C. The origin of a large tensile stress in the film is consistent with a grain boundary model, whilst the observed decrease at 300°C can be ascribed to surface diffusion in the growing film.

Low-temperature Migration of Silicon in Thin Layers of Gold and Platinum

A. HIRAKI, M.-A. NICOLET and J. W. MAYER, *Appl. Phys. Lett.*, 1971, 18, (5), 178-181

A study of solid-solid reactions of Si with 500-2000 Å layers of sputtered Pt indicates that migration of Si atoms into the Pt occurs at the relatively low temperature of 350°C. The migration induces first the formation of Pt₂Si-like compounds and then PtSi.

Coadsorption of Hydrogen and Carbon Monoxide on (111) Platinum

V. H. BALDWIN and J. B. HUDSON, *J. Vacuum Sci. Technol.*, 1971, 8, (1), 49-52

The coadsorption of H₂-CO mixtures (0-100% CO) on the (111) face of a Pt single crystal was studied over a total pressure range of 5×10^{-9} - 5×10^{-7} Torr. Adsorption behaviour is complex, indicating multiple binding sites for both gases, and there is also evidence for the formation of a surface species containing both H and CO. This same species is observed when HCHO is adsorbed directly from the vapour.

The Pt-Ba Constitution Diagram

E. M. SAVITSKII, V. P. POLYAKOVA and E. M. KHORLIN, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1971, (1), 157-159

BaPt₅ and BaPt₂ occur at the Pt end of the Pt-Ba constitution diagram.

The Heats of Formation in the System Gold-Platinum-Palladium

F. H. HAYES and O. KUBASCHEWSKI, *Metal Sci. J.*, 1971, 5, (Jan.), 37-40

Heats of formation obtained by high-temperature adiabatic calorimetry are presented for a wide range of solid Pd-Pt, Au-Pd and Au-Pd-Pt alloys.

Excess partial entropies of the Pd in Pd-Pt alloys are derived from these results and existing activity data.

Alloy Wire, Round 35Pd-30Ag-14Cu-10Au-10Pt-0.8Zn

S.A.E. Aerospace Material Specification AMS 7735, 1970, 3 pp

A specification for a wire of 35%Pd-30%Ag-14%Cu-10%Au-10%Pt-0.8%Zn is given. The allowed variation in composition, the tensile properties, hardness, tolerances and dimensions are laid down.

The Electrical Resistivity of UPt

A. C. LAWSON, *Phys. Lett. A*, 1970, 33A, (4), 231-232

The electrical resistivity of the ferromagnetic compound UPt shows T² behaviour at low temperatures and a large spin-disorder resistivity above the ordering temperature.

A Study of Grain-boundary Grooving at the Platinum/Alumina Interface

M. MCLEAN and E. D. HONDROS, *J. Mater. Sci.*, 1971, 6, (1), 19-24

Grain-boundary grooving at the interface between solid Pt and Al₂O₃ was studied. The Pt/Al₂O₃ interface energy is 1050 erg/cm² at 1400°C. The rate of growth of the grooves shows that volume diffusion is the operative mass transport mechanism at all temperatures considered. Diffusion through the metal is rate-determining at lower temperatures while diffusion through the ceramic phase predominates at higher temperatures.

Precise Measurements of Thermal Conductivity at High Temperatures (100-1200K)

M. J. LAUBITZ and D. L. MCELROY, *Metrologia*, 1971, 7, (1), 1-15

Various steady state methods of measuring thermal conductivity gave results accurate to within $\pm 2\%$. A detailed analysis of results on 10 metals including Au, Pd and Pt is given. Pt:10%Rh-Pt thermocouples were used in the measurements.

Adsorption and Absorption of Hydrogen in Palladium

V. BREGER and E. GILEADI, *Electrochim. Acta*, 1971, 16, (2), 177-190

The equilibrium constant for transfer of H atoms from the surface to the bulk of a Pd membrane was measured. The apparent standard free energy increases linearly up to a constant value. There

are two types of surface site. The transfer is found to be diffusion controlled.

Thermal E.M.F. and Electrical Resistance of Solid Solutions of the Copper-Palladium System

L. A. UGODNIKOVA, N. V. VOLKENSHEIN and YU. N. TSIQVINKIN, *Fiz. Metal. Metalloved.*, 1971, **31**, (3), 543-547

Studies of the temperature dependence of the thermal e.m.f. and electrical resistance of solid solutions of $\text{Cu}_{1-x}\text{Pd}_x$, where x is 0.05, 0.1, 0.2, 0.3, 0.6, 0.8, are interpreted to relate electronic structure to alloy composition.

Spin Waves and Exchange Interactions in Ordered FePd_3 Alloy

B. ANTONINI, R. MEDINA and F. MENZINGER, *Solid State Commun.*, 1971, **9**, (3), 257-260

The acoustical branch of spin waves in ordered FePd_3 was studied by inelastic scattering of polarised neutrons. Experimental results best fit the law $\hbar\omega = Dq^2(1-\beta q^2)$, and from the numerical values of D and β in the framework of the Heisenberg model, exchange interactions are evaluated: $J^{(1)}_{\text{FePd}} = 1.58 \pm 0.17$ meV and $J^{(2)}_{\text{FeFe}} = 6.85 \pm 0.09$ meV.

Critical Behaviour of the Resistivity of a Dilute Pd-Mn Alloy

G. J. NIEUWENHUYIS and B. M. BOERSTOEL, *Phys. Lett. A*, 1970, **33A**, (5), 281-282

Values of the resistivity of 1.0 at.% Mn-Pd are given; they are shown to fit a phenomenological model using a Gaussian distribution of transition temperatures.

Diffusion Studies in the Niobium-Palladium System by Means of the Electron Microprobe

A. BRUNSCH and S. STEEB, *Z. Metallkunde*, 1971, **62**, (3), 247-251

Diffusion processes at 700-1030°C were investigated by means of quantitative electron-probe microanalysis in the system Nb-Pd. The phases NbPd_2 , NbPd_3 , NbPd_4 , NbPd_5 and NbPd_6 were observed. The phase diagram only shows the phases Nb_2Pd , NbPd_2 and NbPd_3 . The partial differential coefficients D_{Nb} and D_{Pd} were determined. The temperature dependency of D_{Nb} is greater than that of D_{Pd} . Both coefficients become equal at a temperature between 900 and 1030°C.

On Some Variants of the NiAs Family in Mixtures of Palladium with B-Elements

M. EL-BORAGY and K. SCHUBERT, *Z. Metallkunde*, 1971, **62**, (4), 314-323

The structure of Pd_5Sb_3 in the system Pd-Sb displays 3 structural variants. The same type of variants have been found in mixtures of the type Pd-B-Te where B=B element. Discussions on

the stability of these phases are based on the 2-electron correlation model for the binding in metallic phases.

On a Quantitative Criterion for Ferromagnetism

G. M. GANDELMAN, N. A. DMITRIEV and M. F. SARRY, *Zh. Eksper. Teor. Fiz.*, 1970, **59**, (6), 2016-2024

Measurement of the energies of a number of metals in the non-magnetic and ferromagnetic states shows that in the case of Ru and Pd both energies are practically the same.

Toward the Superconductivity of Rhodium

A. C. MOTA, W. C. BLACK, P. M. BREWSTER, A. C. LAWSON, R. W. FITZGERALD and J. H. BISHOP, *Phys. Lett. A*, 1971, **34A**, (3), 160-161

Superconducting transition temperatures of Rh-Ir and Rh-Os alloys indicate that the critical temperature of Rh will be 0.2mK.

Very Low Dependence of the Electrical Resistance of $\text{Rh}_{0.99}\text{Fe}_{0.01}$

N. F. OLIVEIRA and S. FONER, *Phys. Lett. A*, 1971, **34A**, (1), 15-16

Measurements of the electrical resistance of $\text{Rh}_{0.99}\text{Fe}_{0.01}$ at 4.2-0.085 K are reported. At lowest temperatures the resistance varies linearly with temperature, and shows no T^2 dependence.

Phase Transformations in Near Equiatomic Ta-Ru Alloys

M. A. SCHMERLING, B. K. DAS and D. S. LIEBERMAN, *Metall. Trans.*, 1970, **1**, (12), 3273-3278

Phase transitions in near equiatomic Ta-Ru alloys were investigated with X-ray powder patterns at room temperature, and resistance, metallography and susceptibility measurements as a function of temperature. The results suggest a 2 step cubic-to-tetragonal-to-orthorhombic martensitic transformation with decreasing temperature in 50-50 at.% alloys; those further away in composition exhibit a single transition from cubic-to-tetragonal.

On the Temperature Dependence of Electrical and Thermal Conductivity of Rhenium and the Metals of the Platinum Subgroup

S. N. L'VOV, P. I. MAL'KO and V. F. NEMCHENKO, *Fiz. Metal. Metalloved.*, 1971, **31**, (1), 108-115

Data for the electrical resistivity and thermal conductivity of Re, Os, Ir, and Pt at 80-1900 and 80-1400 K respectively show that the variations of their temperature dependences are connected with changes to their Fermi surfaces during metal-metal transitions. These metals are compared with Group IV-VI transition metals.

Dental Casting Gold Alloy

ISO Recommendation R 1562

The requirements of the alloy, colour, composition and physical properties are laid out for dental casting gold alloys which contain Pt metals. The

alloys are graded according to their hardness, and a list of physical tests are given to ensure the good quality of the material.

CHEMICAL COMPOUNDS

The Reaction of Selected Lanthanide Carbides with Platinum and Iridium

N. H. KRİKORIAN, *J. Less-common Metals*, 1971, **23**, (3), 271-279

Dicarbides of Y, Ce and Er react with Pt and Ir at 1000-1600°C to form a number of rare-earth platinides and iridides and free C. No ternary compounds were found, but ternary diagrams are constructed theoretically. Lower limits for the free energy of formation of the intermetallic compounds are deduced empirically.

The Kinetics and Equilibria of the Platinum-Chlorine System

A. LANDSBERG and J. L. SCHALLER, *Ibid.* (2), 195-202

The kinetics and vapour-solid equilibria of the Pt-Cl system were studied at 470-880°C at $p_{Cl_2} = 152-760$ Torr; three kinetic regions differentiated by separate controlling mechanisms exist. Correlation is made between the kinetic factors and equilibria involving; the vapour pressure of Pt_6Cl_{12} ; Cl_2 and Pt_6Cl_{12} vapour in equilibrium with Pt; Cl_2 and Pt_3Cl_3 vapour over Pt.

Mono-olefin and Acetylene Complexes of Nickel, Palladium and Platinum

J. M. NELSON and M. B. JONASSEN, *Coordination Chem. Rev.*, 1971, **6**, (1), 27-63

The preparation and properties of zero- and divalent complexes of Pd and Pt are described. The nature of the metal-ligand bond and the use of the complexes in catalysis are discussed.

Some Novel Complexes Including Very Active Hydrogenation Catalysts Formed from Rhodium Trichloride and Tertiary *t*-Butylphosphines

C. MASTERS, W. S. McDONALD, G. RAPER and B. L. SHAW, *Chem. Commun.*, 1971, (4), 210-211

Complexes of the type *trans*- $RhCl_2L_2$, $RhHCl_2L_2$, RhH_2ClL_2 , and *trans*- $RhCl(CO)L_2$ were prepared from tertiary *t*-butylphosphines and $RhCl_3$; some of the complexes are very active hydrogenation catalysts.

Thermodynamics of the System Ruthenium-Oxygen. Determination of the Free Energy of Formation of RuO_2 by Means of e.m.f. Measurements

S. PIZZINI and L. P. ROSSI, *Z. Naturf. A*, 1971, **26**, (1), 177-179

The e.m.f. of the galvanic chain $Pt/Ru \rightarrow RuO_2/ZrO_2-Y_2O_3/O_2(p)/Pt$ was measured between 900

and 1250°C. The results were used to calculate the values of -73.36 kcal/mole for the standard free enthalpy of formation of RuO_2 and -41.88 e.u. for the entropy of the same.

Crystal Growth, Electrical Resistivity and Lattice Parameters of RuO_2 and IrO_2

S. A. BUTLER and J. L. GILLSON, *Mater. Res. Bull.*, 1971, **6**, (2), 81-90

The growth of IrO_2 and RuO_2 single crystals is described. The crystals are generally rod-shaped and extensive twinning is observed. Lattice parameters and residual resistivity ratios are given, but no simple correlation exists between these and growth conditions.

Crystallographic Study of Ru(II) and Ru(III) Hexammine Chlorides

J. TREHOUX, D. THOMAS, G. NOWOGROCKI and G. TRIDOUT, *Bull. Soc. Chim. Fr.*, 1971, (1), 78-80

$Ru(NH_3)_6Cl_2$ crystallises in a cubic cell with $a = 10.035$ Å. $Ru(NH_3)_6Cl_3$ crystallises with a monoclinic cell with $a = 12.7$ Å, $b = 21.6$ Å, $c = 14.1$ Å and $\beta = 122.5^\circ$. A study of this structure suggests it is derived from the f.c.c. structure adopted by similar 6-coordinate complexes.

Transition Metals Groups VIII and IB

Edited by D. SEYFERTH and R. B. KING, *Organomet. Chem. Rev. B, Ann. Surv.*, 1971, **6**, (3)

This issue contains several reviews of the papers on organometallic complexes of the Group VIII and Group IB metals including the Pt metals and Au.

ELECTROCHEMISTRY

The Anodic Oxidation of Platinum: Evidence for a High Field Ionic Conduction Mechanism

J. L. ORD and F. C. HO, *J. Electrochem. Soc.*, 1971, **118**, (1), 46-51

The anodic oxidation of Pt in 1 N H_2SO_4 was studied using open circuit transients to determine Tafel slopes and by following film growth optically with an ellipsometer. The results are interpreted in terms of an ionic conduction model in which overpotential appears across the anodic oxide film; the log of the ionic current density is proportional to the field in the oxide.

Limiting Oxygen Coverage in Platinised Platinum Electrodes

T. BIEGLER, D. A. J. RAND and R. WOODS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **29**, (2), 269-277

The limiting O coverage on platinised Pt electrodes was found to consist of a monolayer of chemisorbed O atoms. Comparison with the charge on a H monolayer showed the stoichiometry of the O layer to be 2 O atoms/surface Pt atom.

Platinum Electrodes and Calcia-stabilised Zirconia

R. J. BROOK, W. L. PELZMANN and F. A. KROGER, *J. Electrochem. Soc.*, 1970, **118**, (2), 185-192

Measurements of the direct current-voltage characteristics of calcia-stabilised ZrO_2 using Pt electrodes of various types were made. The rate limiting steps in the electrical conduction sequence can be: (i) ionic conduction O^{2-} in the ZrO_2 , (ii) electronic conduction in the ZrO_2 , (iii) O atom diffusion through the cathode, (iv) the transfer of O from the gas phase into the ZrO_2 .

The Problem of the Relation of Catalytic Activity of Platinised Platinum Electrode Catalysts to Weight of Platinum Deposit and the Size of Their Surfaces

A. A. SUTYAGINA, I. N. GOLYANITSKAYA and G. P. KHOMCHENKO, *Zh. Fiz. Khim.*, 1971, **45**, (2), 395-399

The activity of electrodeposited Pt catalysts with various amounts of Pt for the reduction of nitromethane is not related to change in the true surface area as measured by H_2 adsorption. One cannot determine specific activity by knowing the true surface area. X-ray and electron microscope studies lead to the conclusion that the change in weight of Pt deposit affects the access of reacting molecules to inner surfaces of the catalysts.

Determining the Stages of Anodic Oxidation of Hydrogen on a Palladium Membrane in Molten Carbonates

N. F. SIZINTSEVA, *Ibid.*, (4), 892-896

Studies of the anodic oxidation of H_2 on Pd membranes at 500-660°C, 1.5 atm H_2 show that maximum oxidation depends on the chemical composition of the Pd surface touching the electrolyte, which consists of the eutectic mixture of Li_2CO_3 , Na_2CO_3 and K_2CO_3 , melting at 397°C. It is concluded that a slow process occurs at the boundary as one stage of the complex anodic oxidation of H_2 , which includes adsorption of H_2 and its diffusion through the membrane.

On the Production of Palladised Palladium Electrodes with Electrochemical Properties

A. V. SHASHKINA, *Ibid.*, (3), 625-629

A method to calculate the energy of bonding of adsorbed H_2 on a Pd electrode is presented and the best conditions for producing Pd electrodes with specified electrochemical properties are recommended.

Adsorption and Catalytic Properties of Palladium-Iridium Electrode Catalysts in Alkaline Medium

A. A. SUTYAGINA, L. G. KOPEVA and G. P. KHOMCHENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1971, **26**, (1), 86-89

Studies of the adsorption and catalytic properties

of Pd, Ir and Pd-Ir electrode catalysts in 0.1 N KOH revealed the effect of Ir on overvoltage of H ionisation and discharge on Pd, and the effect of Ir on the catalytic activity of Pd for reduction of nitromethane.

Adsorption and Catalytic Properties of Platinum-Osmium Electrode Catalysts in 0.1 N Sulphuric Acid Solutions

A. A. SUTYAGINA, I. N. GOLYANITSKAYA, G. P. KHOMCHENKO and G. D. VOVCHENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1970, **25**, (6), 691-695

The adsorption of H_2 and the catalytic activity at Pt-Os alloys depend on the chemical composition and physico-chemical properties of the surface and of the microstructure.

Investigation of Mixed Platinum-Rhodium Electrode Catalysts. Effect of Electrolyte Composition on Adsorption and Catalytic Properties of Alloys

G. S. MANANKOVA, T. M. GRISHINA, G. P. KHOMCHENKO and G. D. VOVCHENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1971, **26**, (1), 115-117

Studies of the effect of electrolyte composition on adsorption and catalytic properties of electrostatically precipitated Pt-Rh showed that the adsorption of H_2 goes through a maximum and also decreases in the order $H_2SO_4 > KOH > HCl > HBr$. Rates of hydrogenation of acroleic acid varied similarly to rates of adsorption of H_2 .

Kinetics of the Reduction of Maleic Acid on Ruthenium Electrode Catalyst

I. V. KUDRYASHOV, A. V. IZMAILOV and D. G. NARYSHKIN, *Zh. Fiz. Khim.*, 1971, **45**, (2), 457-459

The kinetics of the reduction of maleic acid by H_2 on Ru black were studied electrochemically and rate constants and activation energies were calculated.

ELECTRODEPOSITION AND SURFACE COATINGS

Osmium Plating

Electroplating Met. Finish., 1971, **24**, (2), 30

Bright Os can be plated from a salt bath containing equivalent parts of NaCN and KCN with 8% $OsCl_3$ at 1-2 A/dm². The plating must be carried out at $\approx 600^\circ C$, so an inert atmosphere is required.

Borohydrides in the Plating of Plastics

H. NIEDERPRÜM and H.-G. KLEIN, *Metal Finish. J.*, 1971, **17**, (193), 18-24

The uses of amine boranes of general formula $R_3N \cdot BH_3$ (where R = hydrogen and/or a hydro-

carbon radical) in the plating of plastics are reviewed. Amine boranes are particularly useful for sensitising the surface with Pd ions prior to plating.

LABORATORY APPARATUS AND TECHNIQUE

An Inductive Water Thermostat Using On-Off Triac Control and Platinum Sensing

J. M. DIAMOND, *Rev. Sci. Instrum.*, 1971, **42**, (1), 134-140

Sensing in an on-off thermostat is provided by a very low resistance Pt coil in direct contact with the water, thus providing quick response, stability and, because of the transformer-coupled circuit used with this probe, the possibility of very good insulation.

Electrochemical Detection of H₂, CO, and Hydrocarbons in Inert or Oxygen Atmospheres

A. B. LA CONTI and H. J. R. MAGET, *J. Electrochem. Soc.*, 1971, **118**, (3), 506-510

An electrochemical sensor for qualitatively detecting H₂ in gas mixtures containing electrochemically inert species is described. Limiting diffusion current measurements in the range +0.25 to 0.65V vs a Pt electrode in the same acid solution are proportional to the H₂ content of the bulk phase. When an active species is present the H₂ content is found by keeping a working electrode potential of +1.06V at which H₂ is immediately ionised.

A Four Probe Cell for Resistivity Measurements at Temperature Independent Pressures

S. D. HOTTMAN and H. A. POHL, *Rev. Sci. Instrum.*, 1971, **42**, (3), 387-388

A cell is described which permits resistivity, Hall effect and related determinations to be made at constant high pressures and over a wide temperature range. The cell contains four Pt probes, B & S No. 32 wire spaced equidistantly round the edge of the lower anvil. This gives inherent precision, minimises electrode junction problems and permits precise determination of a wide range of resistivities.

HETEROGENEOUS CATALYSIS

On the Mechanism of Carbon Monoxide Oxidation. Part I. Determination of the Stoichiometric Number of the Rate-determining Step on a Platinum Catalyst by Means of a Carbon-14 Tracer

S. OKI and Y. KANEKO, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1970, **18**, (2), 93-114

The reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ catalysed by Pt

was investigated at 300-474°C and 125 mm Hg using C¹⁴ as a tracer. The results show that the rate determining step switches from O₂→2O(a) to CO + O(a)→CO₂ when the temperature rises above 400°C.

Catalytic Oxidation of Methanol over Platinum

J. G. FIRTH, *Trans. Faraday Soc.*, 1971, **67**, (1), 212-215

The complete oxidation of methanol vapour over Pt was studied. Results indicate two parallel reaction mechanisms, one of which is inhibited by O₂. Derived activation energies indicate the inhibited reaction involves the breaking of an O-metal bond in the rate determining step.

Hydrogenation of Benzene and Isoprene on Platinum/Alumina Catalysts Modified by Manganese and Chromium

O. V. ANDREEVA, R. G. DAVLESUPOVA, V. V. BORISOVA and R. I. IZMAILOV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (3), 569-572

An addition of one part of Mn to ten of Pt in Pt/Al₂O₃ raised the catalytic activity during C₆H₆ hydrogenation and diminished the effect of thiophene poisoning. A similar addition of Cr reduced the activity and stability during poisoning by thiophene. Additions of Mn or Cr increased the catalytic activity during liquid-phase low-temperature hydrogenations of isoprene.

On Stages of the Mechanism of Aromatisation of N-Hexane in the Presence of Platinum/Alumina and Palladium/Alumina Catalysts

B. A. KAZANSKII, V. S. FADEEV and I. V. GOSTUNSKAYA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (4), 677-681

Aromatisation of N-C₆H₁₄ over 0.6% Pt/Al₂O₃ and 0.6% Pd/Al₂O₃ takes place by C₆- and C₅-dehydrocyclisation. C₆-dehydrocyclisation is the principal mechanism over Pd/Al₂O₃. There is more C₆-dehydrocyclisation followed by dehydroisomerisation when Pt/Al₂O₃ is used. C₆-dehydrocyclisation of N-C₆H₁₄ over both catalysts represents successive dehydrogenations to form mono-olefins, dienes and trienes, all of which are readily converted into aromatic hydrocarbons.

On Ways of Converting Cyclohexane and Cyclohexene in Reforming Conditions on Bifunctional Catalysts

M. A. RYASHENTSEVA, KH. M. MINACHEV and V. I. AVAEV, *Neftekhimiya*, 1971, **11**, (1), 12-17

Conversions of cyclohexane and cyclohexene on Pd/Al₂O₃ and Pt/Al₂O₃ were studied in reforming conditions with poisoning by thiophene and subsequent reduction by hydrocarbons. The dehydration functions of Pd/Al₂O₃ were more sensitive to poisoning by cyclenes and thiophene

than were those of Pt/Al₂O₃. Cyclohexane and cyclohexene evidently are converted to methylcyclopentane and benzene in different ways, probably via different intermediates.

The State of Platinum on Reforming Catalysts

F. FIGUERAS, B. MENCIER, L. DE MOURGES, C. NACCACHE and Y. TRAMBOUZE, *J. Catalysis*, 1970, **19**, (3), 315-321

The dispersion of Pt on a series of SiO₂-Al₂O₃ supports with different Al₂O₃ contents was found to be constant. The catalytic activity for cyclohexane dehydrogenation increased when the Al₂O₃ content decreased. The activity for tert-butanol dehydration and for perylene cation formation decreased when Pt was deposited on the support. The results were explained by a charge transfer complex between the metal and the oxidising sites of the support.

Study of Metal Catalysts by Temperature Programmed Desorption. II. Chemisorption of Hydrogen on Platinum

S. TSUCHIYA, Y. AMENOMIYA and R. J. CVETANOVIC, *Ibid.*, 245-255

The chemisorption of H₂ on a Pt black catalyst was investigated at -196 to 400°C by a temperature programmed desorption technique. Four types of chemisorbed species were indicated (α , β , γ and δ). α is the weakest chemisorbed species, γ and δ are the strongest. The four forms are interrelated so that one retards chemisorption of the others. They are assigned to four adsorption forms, two atomic and two molecular.

Ibid. III. Hydrogen-Deuterium Exchange on Platinum

Ibid., 1971, **20**, (1), 1-9

H-D surface exchange was investigated at -76 to -195°C between D₂ (or H₂) preadsorbed on the Pt surface and H₂ (or D₂) in the gas phase. Isotopic equilibration of gaseous mixtures of H₂ and D₂ occurred much faster than the surface exchange, the former occurring even at -195°C. The results suggest H molecules chemisorbed in a linear form may take part in isotopic exchange.

Some Problems of the Kinetics of Hydrogenolysis of Cyclopentane Hydrocarbons on Platinised Charcoal. Part 3. Selectivity of Hydrogenolysis of 1,2- and 1,3-Dimethylcyclopentanes in Conditions of Pulsed Operation and Flow Method

O. V. BRAGIN, T. G. OLFER'EVA, A. V. KAZANSKAYA-KOPERINA and A. L. LIBERMAN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (4), 704-710

The apparent activation energy for hydrogenolysis of *cis*-1,3-dimethylcyclopentane is similar to that for other cyclopentanes and lies in the range 36.5-43 kcal/mole, according to which bond of the cyclopentane ring is affected.

The Structure and Activity of Supported Metal Catalysts. V. Variables in the Preparation of Platinum/Silica Catalysts

T. A. DORLING, B. W. J. LYNCH and R. L. MOSS, *J. Catalysis*, 1971, **20**, (2), 190-201

A study of the variables involved in preparing Pt/SiO₂ catalysts by impregnation with H₂PtCl₆ or by adsorption of Pt amines from solution was made. A model of the impregnation process is used to explain the variation in Pt area and crystallite size with Pt content; the adsorption of Pt(NH₃)₄²⁺ from solution is related to the number of available exchange sites on SiO₂ with different areas. Firing in air is discussed.

Hydrogenation of Benzene Containing Sulphur Compounds in the Presence of Palladium Catalysts

A. V. LOZOVOL, D. P. PHELINA, S. A. SENYAVIN and V. I. SIN'KO, *Neftekhimiya*, 1971, **11**, (2), 172-178

Studies of hydrogenation of C₆H₆ containing 0.005% each of thiophene and CS₂ at 270°C, 100 atm over 1.5, 3.0 and 4.5% Pd/ γ -Al₂O₃ treated with H₂S showed that only 4.5% Pd/Al₂O₃ is stable. It is slowly reversibly deactivated during C₆H₆ hydrogenation but maintains its activity for hydrogenolysis of thiophene and CS₂. Catalyst activity is completely abated and the C₆H₆ is reduced to cyclohexane by repeated hydrogenations over the partially deactivated catalyst. 50 atm is insufficient to maintain the activity and stability of Pd catalysts for hydrogenation of C₆H₆ containing S compounds. It is proposed to produce cyclohexane by the two-stage hydrogenation of C₆H₆ containing thiophene and CS₂ over Pd/ γ -Al₂O₃.

Selective Hydrogenation of Mesityl Oxide to Methyl Isobutyl Ketone

V. MACHO, *Chem. Průmysl*, 1971, **21**, (1), 9-11

Mesityl oxide was hydrogenated on Pd/Al₂O₃ at 40-220°C to methyl isobutyl ketone. The selectivity was 92-99%. When the molar ratio H/mesityl oxide was 5, hydrogenation followed first order kinetics. The activation energy is 19.8 ± 1.1 kcal/mole.

Dehydrocyclisation of N-Heptane and 2,4-Dimethylpentane in the Presence of Palladium/Alumina Catalyst

B. A. KAZANSKII, I. V. GOSTUNSKAYA, L. S. SOLONINA and V. S. FADEEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (4), 682-685

Yields of aromatic hydrocarbons in the presence of 0.6% Pd/Al₂O₃ in a stream of H₂ at 1 atm, 400-520°C in a pulsed set-up is twice as great from N-C₇H₁₆ as from 2,4-dimethylpentane. C₇H₁₆ formed alkylcyclopentanes. The amount of C₅-dehydrocyclisation was almost the same for both paraffins. Ethylcyclopentane, 1,2- and 1,3-dimethylcyclopentane formed by C₅-dehydrocyclisation of C₇H₁₆ are all dehydroisomerised to C₆H₅CH₃.

Physico-chemical Characteristics of Pd/BaSO₄ Catalysts

A. M. SOKOL'SKAYA, F. B. BIZHANOV, A. M. KHISAMETDINOV, S. A. RYABININA and K. K. KUZEMBAEV, *Zh. Fiz. Khim.*, 1971, **45**, (1), 83-85

Electron microscope and X-ray studies of finely dispersed 5% Pd/BaSO₄ and Rh/BaSO₄ used in hydrogenations of multiple bonds did not reveal the Pd and Rh which form the active part of these catalysts, which have high activity for hydrogenation of phenylacetylene.

The Reaction of 1-Tetralones with Palladium/Carbon

J. M. SPRINGER, C. W. HINMAN, E. J. EISENBRAUN, P. W. FLANAGAN, M. C. HAMMING and D. E. LINDER, *J. Org. Chem.*, 1971, **36**, (5), 686-689

The dehydrogenation of 1-tetralone [3,4-dihydro-1(2H)-naphthalenone] and similar α , β unsaturated ketones when carried out at 260°C, in the absence of a solvent, and over a Pd/C catalyst gave arenes as the main product instead of the usual phenolic products.

Hydrogenolysis of Cyclopropanes

A. L. SCHUTZ, *J. Org. Chem.*, 1971, **36**, (3), 383-386

Cyclopropane derivatives with unsaturated functional groups were subjected to hydrogenolysis at room temperature and 1 atmosphere over a Pd/C catalyst. Exclusive C₁-C₂ bond cleavage was observed for all cyclopropylmethyl ketones studied, and was predominant for cyclopropane carboxylic acids and esters.

Hydrogenation of Acetylenic Compounds. VIII. Effect of Temperature and Partial Hydrogen Pressure on the Rate and Selectivity of 2-Butyne-1,4-diol Hydrogenation on a Pd/CaCO₃ Catalyst

G. V. MOVSISYAN, G. A. CHUKHADZHANYAN and T. A. AZOVTSOVA, *Arm. Khim. Zh.*, 1970, **23**, (6), 566-567

Studies of the effects of temperature and P_{H_2} on the rate and mechanism of hydrogenation of 2-butyne-1,4-diol on 5% Pd/CaCO₃ in aqueous and alcoholic solutions show that the rates of hydrogenation of C \equiv C and of the formed C=C are first order in H₂ with maximum rate at 60°C. Tar formation occurs at higher temperatures. C=C is hydrogenated faster than C \equiv C above 0°C; below 0°C the reverse is true. No tar forms at <0°C.

Cyclopropane-Hydrogen Reaction over the Group VIII Noble Metals

R. A. DALLA BETTA, J. A. CUSUMANO and J. H. SINFELT, *J. Catalysis*, 1970, **19**, (3), 343-349

The specific catalytic activities of the Group VIII noble metals were determined for the hydrogenation of cyclopropane to C₃H₆. On Ru and Os a fragmentation reaction giving CH₄ and C₂H₆

also occurred. For the metals the order of activities is Pt > Ir > Os and Pd > Rh > Ru.

Hydrogenolysis of *n*-Heptane over Unsupported Metals

J. L. CARTER, J. A. CUSUMANO and J. H. SINFELT, *Ibid.*, 1971, **20**, (2), 223-229

The hydrogenolysis of *n*-heptane was investigated on Pd, Rh, Ru, Pt and Ir powders. Hydrogenolysis was predominant for all metals except Pt, on which isomerisation and dehydrocyclisation were observed. The order of activities corresponds to the *d* character of the metallic bond. Pd and Rh cracked the terminal C-C bond, while the other metals were less selective.

Processing Nitric Acid Tail Gas

O. J. ADLHART, S. G. HINDIN and R. E. KENSON, *Chem. Engng. Prog.*, 1971, **69**, (2), 73-78

The use of spherical and honeycomb catalysts of Pt, Rh and Pd for abating N oxides in HNO₃ tail gas is described. The former have a longer life and are more reliable but require a high pressure drop and special vessel design. The latter can be used with a smaller, less expensive vessel.

Adsorption of Hydrogen on Hydrogenation Catalysts in Solutions. VI. Adsorption and Heat of Adsorption of Hydrogen on Rh Black

YU. A. PODVYAZKIN and G. P. GRECHUSHKINA, *Zh. Fiz. Khim.*, 1971, **45**, (4), 908-911

Charging curve studies of H₂ adsorption on Rh black in 0.1 N H₂SO₄, 0.9 N NaCl + 0.1 N H₂SO₄ and 0.1 N KOH at 0-50°C were used to derive the differential heat of adsorption as a function of surface coverage.

VII. Adsorption and Heat of Adsorption of Hydrogen on Ir Black in 0.1 N H₂SO₄, 0.1 N HCl and 0.1 N KOH Solutions

Ibid., 912-915

Charging curve studies of H₂ adsorption on Ir black in 0.1 N H₂SO₄, 0.1 N HCl and 0.1 N KOH at 0-50°C were used to derive differential heats of adsorption to compare with earlier work.

On the Catalytic Activity and Selectivity of Homogeneous and Heterogeneous Rhodium Catalysts in Hydrogenation and Isomerisation Reactions

L. KH. FREIDLIN, E. F. LITVIN and L. F. TOPURIDZE, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, (2), 404-408

The addition of H₂ at double bonds, the ratio of the rates of isomerisation and hydrogenation of C=C bonds and the selectivity of these processes were not related to the phase state of the catalysts when Rh catalysts were studied for these reactions with isoprene and pentene-1. Catalysts were Rh black, Rh/C, Rh/Al₂O₃, and complexes of Rh with *N*-phenylanthranilic acid and with *L*-tyrosine.

Characteristics of Ir Catalyst Surfaces by Gas Chemisorption

C. S. BROOKS, *J. Colloid Interface Sci.*, 1970, **34**, (3), 419-427

Chemisorption of H₂ and O₂ at room temperature on Ir/Al₂O₃ catalyst was studied. The surface coverage by IrO₂, stoichiometry for H₂ and O₂ reactions with Ir and surface coverage with species other than O₂ were measured.

Stereochemistry of Some Catalytic Conversions of Cyclic Hydrocarbons in the Presence of Group VIII Noble Metals

O. V. BRAGIN and A. L. LIBERMAN, *Uspekhi Khim.*, 1970, **39**, (12), 2122-2153

Stereochemistry of heterogeneous catalytic hydrogenations of dialkylcycloolefins and di- and polyalkylbenzenes was considered for Group VIII noble metal catalysts, including the isomerisation of di- and polyalkylcyclohexanes. The latter reaction appears to be mono- but is really bimolecular.

HOMOGENEOUS CATALYSIS

Isomerisation of Olefins under the Action of Palladium Salts

A. A. GRIGOR'EV, M. YA. KLIMENKO and I. I. MOISEEV, *Neftekhimiya*, 1971, **11**, (2), 182-188

The effects of alcoholic and hydrocarbon solvents and of olefin oxidation catalyst components were demonstrated during isomerisations of hexene-1, 4-methylpentene-1 and 2-methylpentene-1 using the usual form of PdCl₂. If this catalyst is heated above 403°C the high temperature polymorphic form of PdCl₂ is produced. This gives increased activity for olefin isomerisation.

Palladium-catalysed Hydrosilation of Olefins and Polyenes

M. HARA, K. OHNO and J. TSUJI, *J. Chem. Soc., D, Chem. Commun.*, 1971, (6), 247

Pd compounds and metallic Pd are active catalysts for the hydrosilation of olefins and polyenes in the presence of ligands such as PPh₃.

New Cyclisation Reaction of Conjugated Dienes with Isocyanate Catalysed by Palladium Complexes

K. OHNO and J. TSUJI, *Ibid.*, 247-248

Novel 2:1 cocyclisation reactions of conjugated dienes, e.g. butadiene, with isocyanate to give divinylpiperidones are reported. The reactions are catalysed by Pd-PPh₃ complexes.

Syntheses of Long-chain Amines by Palladium Telomerisation of Butadiene

T. MITSUYASU, M. HARA and J. TSUJI, *Ibid.*, (7), 345
Novel syntheses of long-chain amines by the Pd acetate or PdCl₂(PPh₃)₂ catalysed telomerisation of butadiene with NH₃ and nitroalkanes followed by hydrogenation are reported.

Asymmetric Homogeneous Hydrogenation with Rhodium(I) Complexes of Chiral Phosphines

J. D. MORRISON, R. E. BURNETT, A. M. AGUIAR, C. J. MORROW and C. PHILLIPS, *J. Am. Chem. Soc.*, 1971, **93**, (5), 1301-1303

Reduction of (E)-β-methylcinnamic acid in a 1:1 benzene-ethanol solution of prerduced tris-(neomenthylphenylphosphine)Rh(I)chloride was carried out. The product was 3-phenylbutanoic acid with 61% enantiomeric excess of the S isomer. This is probably the highest degree of asymmetric bias accomplished with a chiral hydrogenation catalyst.

Organometallic Compounds in Synthesis. II. Further Applications of Tris(phenylphosphine)chlororhodium

A. J. BIRCH and K. A. M. WALKER, *Aust. J. Chem.*, 1971, **24**, (3), 513-520

RhCl(PPh₃)₃ is shown to have advantages over heterogeneous catalysts where it is applicable. Uses are discussed in the syntheses of new compounds in improvements in synthetic routes. The hydrogenation of butadiene rubbers is reported.

FUEL CELLS AND BATTERIES

Fluidised-bed Fuel-cell Electrodes

T. BERENT, R. MASON and I. FELLS, *J. Appl. Chem. Biotechnol.*, 1971, **21**, (3), 71-76

Anodic and cathodic fluidised-bed fuel cell electrodes which operate with dissolved reactants were studied. The beds consist of glass beads; the anode beads were coated with a Pt-Ru alloy catalyst or with Pt directly. For the anode beds the apparent polarisation increased with increase in fluidisation, due to an increased bed resistance.

CATHODIC PROTECTION

Electrochemical Corrosion Control in Effluent Treatment Plant

K. G. C. BERKLEY, *Chem. & Ind.*, 1971, (11, Mar. 13), 287-294

A general account of the mechanism of electrochemical corrosion is given with various methods of cathodic protection. Impressed current anodes, including Pt/Ti and Pt/Ta are described. Their properties, uses and advantages are discussed.

CHEMICAL TECHNOLOGY

Economics of Dimensionally Stable Anodes

J. HORACEK and S. PUSCHAVER, *Chem. Engng. Prog.*, 1971, **67**, (3), 71-74

The use and advantages of dimensionally stable anodes of oxides of the Pt metals on Ti substrates are described. They are more efficient and more

economical than graphite anodes as the investment and operating costs are lower and they use less electricity. They also give a purer product.

ELECTRICAL AND ELECTRONIC ENGINEERING

Thick-film Conductor Adhesion Reliability

W. A. CROSSLAND and L. HAILES, *Solid State Technol.*, 1971, 14, (2), 42-47

The degradation of adhesion of soldered Pd containing thick-film conductors on exposure to high temperatures was examined. A mechanism is proposed. Adhesion degradation can be reduced by proper choice of materials and processing conditions.

Process and Performance Characteristics of "Birox" Thick-film Resistor Compositions

L. C. HOFFMAN and M. J. POPOWICH, *Solid State Technol.*, 1971, 14, (1), 33-37

A review of the properties of the "Birox" thick-film resistor compositions which contain Pd, Au and Ag is given. The effect of variations in the firing temperature and time, type of termination material and resistor geometry on key electrical properties is discussed.

NEW PATENTS

METALS AND ALLOYS

Dispersion Hardening of Metals

JOHNSON MATTHEY & CO. LTD

U.S. Patent 3,547,712

The mechanical properties of dispersion hardened noble metals or copper are improved by cold working and annealing. The extent of cold working is such that recrystallisation during annealing gives an elongated grain structure highly oriented in the direction of working. Typically the method is applied to Pt or Pt-Rh alloys containing dispersed TiC.

Platinum-Rhodium-Gold Alloys

JOHNSON MATTHEY & CO. LTD

Dutch Appl. 70,08,179

Alloys able to withstand attack by molten glass contain 9-25% Rh, 1-4 wt.% Au and the remainder Pt.

Alloys Containing Pt Group Metals

JOHNSON MATTHEY & CO. LTD

Italian Patent 842,682

A method of making alloys of one or more Pt metals with up to 20 at.% Sc, Ti, V, Y, Zr, Nb, Hf, Ta, or a rare earth metal is described. The Pt metal is melted in a crucible in an Ar atmos-

The Formation and Degradation of Ti-Ag and Ti-Pd-Ag Solar Cell Contacts

Conf. Record of 8th IEEE Photovoltaic Specialists Conf., Seattle, 4-6 Aug. 1970, 40-50

The structure of Ti-Ag and Ti-Pd-Ag solderless solar cell contacts were evaluated before and after 80°C, 95% relative humidity exposure. The contacts were found to contain TiH₂ and undergo structure changes in HT-HH environments which render them unstable.

TEMPERATURE MEASUREMENT

Low Temperature Thermometry in High Magnetic Fields. II. Germanium and Platinum Resistors

L. J. NEURINGER, A. J. PERLMAN, L. G. RUBIN and Y. SHAPIRA, *Rev. Sci. Instrum.*, 1971, 42, (1), 9-14

The effect of static magnetic fields up to 210 kG on the characteristics of commercial Ge and Pt resistance thermometers was measured at 3.5-78 K. Measurements of the transverse and longitudinal magnetoresistance were taken. For Pt thermometers the magnetoresistance above 30 K is small enough for it to become practical to correct for it.

phere; the crucible is evacuated when the base metal is added. Rh-Pt-Zr alloys are particularly mentioned.

CHEMICAL COMPOUNDS

Hexaruthenium Octadecacarbonyl

LONZA LTD

U.S. Patent 3,542,513

Ru₆(CO)₁₈ is obtained by heating [Ru(CO)₄]₃ in a substantially O₂-free atmosphere at 150-250°C and maintaining the CO partial pressure during the reaction at 0.2-2 atm.

Production of Allyl Ruthenium Tricarbonyl Halides

LONZA LTD

U.S. Patent 3,546,264

The production of π-allyl Ru tricarbonyl halides is based on the reaction of [Ru(CO)₄]₃ with allyl halides in an inert solvent under an inert atmosphere. They are used as carbonylation catalysts.

ELECTROCHEMISTRY

Electrolytic Cell

ADMIRALTY MATERIALS LABORATORY

British Patent 1,218,038

In a brine electrolysis cell, one electrode is made